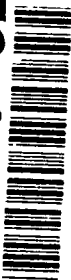


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Semi-Annual Report

Atomic Layer Epitaxy Group IV Materials: Surface Processes, Thin Films, Devices and Their Characterization

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| 13. ABSTRACT (Maximum 200 words) The maximum temperature at which self-terminating monolayers of Si can be formed on Si(100) from Si ₂ H ₆ has been determined to be 570°C. As such, the chemical reactivity of C ₂ H ₄ has been determined to be insufficient at this temperature, and acetylene has been selected as the successor C precursor due to its superior reactivity and chemisorption properties. A cryogenic purifier for removing acetone has been commissioned. Trenched Si(100) wafers are also being made to assess the ALE process for sidewall deposition uniformity and future bipolar devices. Nonstoichiometric, Si-rich SiC has been produced with an associated decrease in the band gap. An AES/XPS UHV analytical system and associated ALE deposition system has been commissioned and integrated into a much larger surface science system. These dual systems will allow a thorough study and characterization of the both the initial nucleation of SiC and the overall ALE growth process of SiC. Tetramethylsilane and hexamethyldisilane have been deposited onto Si substrates in a hot filament CVD chamber to investigate their ability to promote ALE of diamond under DC biasing and a variety of system parameters. An electron gun and heating stage has been added to the growth chamber to enable AES and substrate heating. Good quality diamond films have been nucleated on deposited interlayers of both precursor compounds. The films have been examined by SEM and Raman spectroscopy. Good quality epitaxial films of CeO ₂ have been grown on Si(111) using laser ablation. Atomically clean substrates and slow growth rates were determined necessary for epitaxy. | | | | | |
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I. Introduction

Atomic layer epitaxy (ALE) is the sequential chemisorption of one or more elemental species or complexes within a time period or chemical environment in which only one monolayer of each species is chemisorbed on the surface of the growing film in each period of the sequence. The excess of a given reactant which is in the gas phase or only physisorbed is purged from the substrate surface region before this surface is exposed to a subsequent reactant. This latter reactant chemisorbs and undergoes reaction with the first reactant on the substrate surface resulting in the formation of a solid film. There are essentially two types of ALE which, for convenience, shall be called Type I and Type II.

In its early development in Finland, the Type I growth scenario frequently involved the deposition of more than one monolayer of the given species. However, at that time, ALE was considered possible only in those materials wherein the bond energies between like metal species and like nonmetal species were each less than that of the metal-nonmetal combination. Thus, even if multiple monolayers of a given element were produced, the material in excess of one monolayer could be sublimed by increasing the temperature and/or waiting for a sufficient period of time under vacuum. Under these chemical constraints, materials such as GaAs were initially thought to be improbable since the Ga-Ga bond strength exceeds that of the GaAs bond strength. However, the self-limiting layer-by-layer deposition of this material proved to be an early example of Type II ALE wherein the trimethylgallium (TMG) chemisorbed to the growing surface and effectively prevented additional adsorption of the incoming metalorganic molecules. The introduction of As, however caused an exchange with the chemisorbed TMG such that a gaseous side product was removed from the growing surface. Two alternating molecular species are also frequently used such that chemisorption of each species occurs sequentially and is accompanied by extraction, abstraction and exchange reactions to produce self-limiting layer-by-layer growth of an element, solid solution or a compound.

The Type II approach has been used primarily for growth of II-VI compounds [1-13]; however, recent studies have shown that it is also applicable for oxides [14-18], nitrides [19], III-V GaAs-based semiconductors [20-33] and silicon [34-36]. The advantages of ALE include monolayer thickness control, growth of abrupt interfaces, growth of uniform and graded solid solutions with controlled composition, reduction in macroscopic defects and uniform coverage over large areas. A commercial application which makes use of the last attribute is large area electroluminescent displays produced from II-VI materials. Two comprehensive reviews [37,6], one limited overview [38] and a book [39] devoted entirely to the subject of ALE have recently been published.

The materials of concern in this program include silicon carbide (SiC), diamond (C) and cerium dioxide (CeO₂). Deposition of all three materials has been achieved using the progressive decomposition of metal-organic precursors (SiC and diamond) and laser ablation

(CeO₂). In addition, an XPS/Auger system has been commissioned to fully study the chemistry of the ALE growth cycle for SiC. Nonstoichiometric, Si-rich, SiC has also been produced with an associated shift in the band gap to smaller values.

The following sections introduce each topic, detail the experimental approaches, report the results to date and provide a discussion and a conclusion for each material. Each major section is self-contained with its own figures, tables and references.

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II. Experimental Investigations Leading to the Atomic Layer Epitaxy of Silicon Carbide Thin Films

A. Introduction

All of the common polytypes of silicon carbide possess many physical properties that are very appealing to engineers of electronic devices. This material is well suited to high-power, -speed and -temperature applications because of its high junction breakdown electric field of 5×10^6 V/cm [1], high-saturated electron drift velocity of 2×10^7 cm/s for 6H [2], wide bandgap of 2.2 eV for 3C [3] and high thermal conductivity of 3.5 w/cm°C [4]. In addition to electronic applications, SiC enjoys potential in optoelectronics where blue light emitting devices are possible and have been constructed [5]. These features make SiC an appealing semiconductor material.

Integration of SiC into existing device manufacturing processes would be greatly facilitated by the development of a technology with the ability to deposit uniform layers of SiC on Si substrates. Although chemical vapor deposition, (CVD), has been employed for depositing SiC on Si substrates, deposition of good quality material involves an initial carbonization step and high growth temperatures, both steps would be detrimental to device properties. Atomic layer epitaxy, (ALE), has been employed to deposit SiC films on Si without resorting to carbonization steps or extreme growth temperatures. In addition ALE suggests the capability of depositing films over non-planar substrates with excellent uniformity and step coverage. Development of the ALE technique in reference to SiC deposition may encourage the incorporation of SiC's superior properties into the existing Si-based technology.

The objective of this research is to extend the state-of-the-art regarding SiC thin films via the employment of atomic layer epitaxy (ALE) to deposit the material on selected substrates in a layer-by-layer process. During this reporting period, two key factors in the deposition of SiC were evaluated; the minimum temperature to decompose Si_2H_6 on the $\alpha(6\text{H})\text{-SiC}(0001)$ surface and the suitability of C_2H_4 for performing self-terminating ALE of SiC. In addition, work has begun purifying acetylene gas for use in ALE, a process for producing trench Si substrates to study the deposition of SiC in trenches has been started and preliminary work with non-stoichiometric SiC is underway.

B. Experimental Procedure

ALE Reactor. The ALE system used in this research has been described in detail in previous reports (December, 1991 and June, 1992) and is pictured in Fig. 1. Results of work performed in this reactor with the SiC and the GaN systems are reported elsewhere [6,7]. The ALE reactor has been reconfigured to allow the introduction of triethylaluminum and ammonia as shown in Fig. 2. This modification allows n- and p-type doping of SiC films and permits deposition of AlN and AlN/SiC structures. Within the reactor, rotating samples are alternately exposed to process gases to accomplish deposition in a layer-by-layer process. An additional

feature of the reactor is the tungsten filaments used to decompose ammonia and to aid in deposition of SiC.



Figure 1. ALE system for deposition of compound semiconductors.

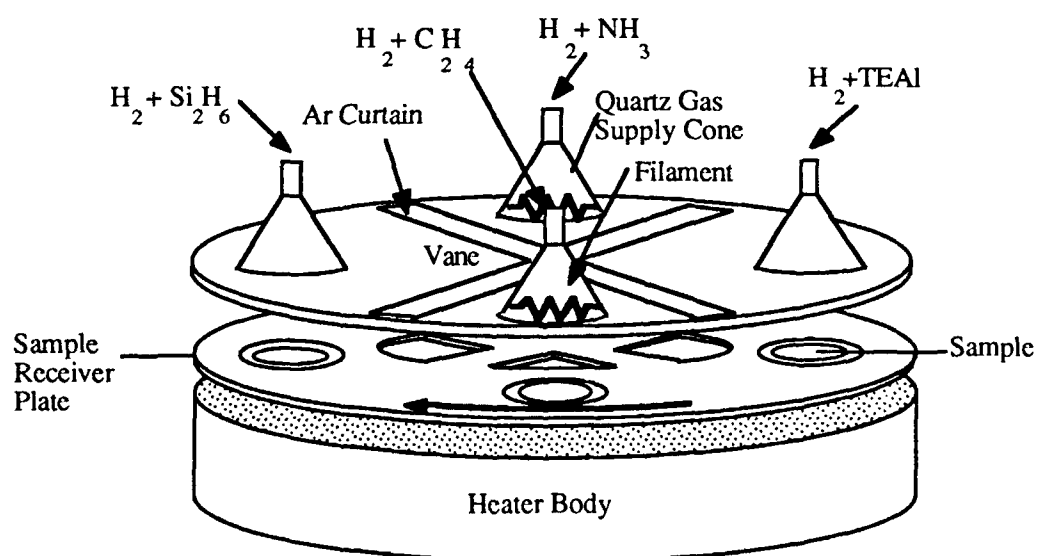


Figure 2. Internal components of ALE reactor.

True ALE of SiC. Previously reported work was based on layer-by-layer deposition of SiC, that is the amount of material deposited per gas cycle was not strictly self limiting at the monolayer level as would be expected in a true ALE process. Although we know that the conversion of adsorbed Si to SiC is self-limiting [7], the decomposition of Si_2H_6 on the Si substrate and on the growing SiC film is pyrolytic at the temperatures employed. The higher temperatures are required due to the difficulty in reacting C_2H_4 at low temperatures. During this reporting period the focus has shifted producing films in a true ALE process with chemically self-terminating monolayers. In pursuit of this goal, several tasks were defined: find the minimum temperature at which Si_2H_6 will decompose on SiC, try to deposit SiC from Si_2H_6 and C_2H_4 under these conditions, assessing the suitability of C_2H_4 for ALE of SiC and choose and prepare another C-containing gas if C_2H_4 is unsuitable.

Minimum decomposition temperature of Si_2H_6 on $\alpha(6\text{H})\text{-SiC}(0001)$ surface. To determine a "temperature ceiling" for ALE of SiC using Si_2H_6 several $\alpha(6\text{H})\text{-SiC}(0001)$ wafers were exposed to a Si_2H_6 flux at temperatures of 245, 300, 340, 430, 520 and 620°C. X-ray photoelectron spectroscopy (XPS) was employed to analyze samples for Si-Si bonding. In addition optical observation proved sufficient to detect the presence of a Si film on the substrates in some cases.

Low temperature deposition of SiC. In the attempt to deposit SiC at temperatures around the minimum decomposition temperature for Si_2H_6 a new rotational pattern was developed. It was found that after exposure to the tungsten filament the substrate surface temperature increased and required a finite amount of time to cool to the general growth temperature. To accommodate this factor, the sample had long pauses under Ar after exposure to the filament and source gases, the new rotational scheme is represented in Fig. 3.

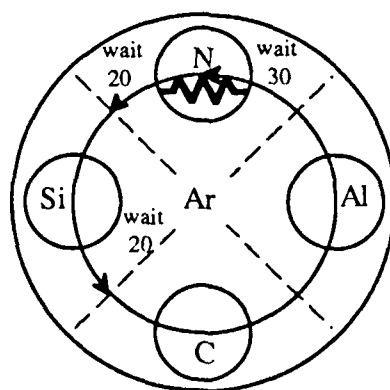


Figure 3. Low temperature rotational scheme.

For low temperature deposition the sample begins at the filament, rotates 45° counter-clockwise (ccw) and resides under Ar for 20 sec., the sample then rotates another 90° ccw through the Si₂H₆ zone and stops under Ar again for 20 sec. and finally the sample rotates through the C₂H₄ zone to return to the filament where it remains for 30 sec. This rotational scheme was employed for deposition runs at sample temperatures from 500 to 800°C. Resulting films were analyzed with Reflection High Energy Electron Diffraction (RHEED).

Preparation of purified acetylene. It was apparent that C₂H₄, ethylene, was not a suitable gas for performing ALE with self-terminating Si layers. The difficulty lies in the low reactivity of ethylene on a Si or SiC surface at low temperatures. Acetylene was chosen as a successor gas due to its superior adsorptive and decomposition properties on Si relative to ethylene. It has been reported that while ethylene chemisorbs and desorbs molecularly on Si, only ≈5% of the acetylene chemisorbed on Si desorbs molecularly while the remaining acetylene undergoes dehydrogenation, producing C on the surface and subsequently SiC [9].

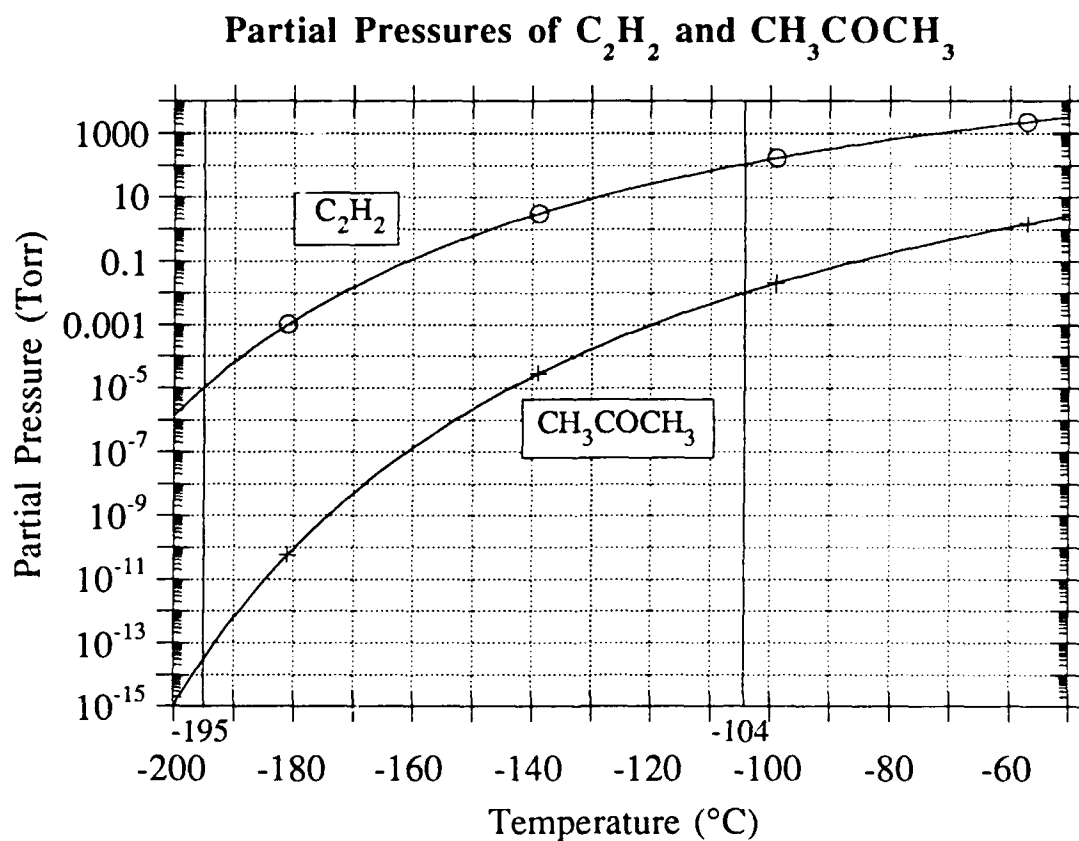


Figure 4. Vapor pressure curves for acetylene and acetone.

A difficulty arises in the fact that since acetylene is violently unstable at pressures above 15 psig it is shipped dissolved in acetone as a stabilizer and to increase capacity of cylinders. Before acetylene would be useful in ALE, the acetone must be removed. One way of separating the acetone could use the disparity between acetylene and acetone's vapor pressures depicted in Fig. 4. A cryogenic distillery depicted in Fig. 5 has been constructed, and several test batches of purified acetylene produced for analysis. During purification, the first of the purifiers two cylinders is filled to ≈ 10 psig with raw acetylene which is then cooled in a LN2 bath. A vacuum is applied to the cooled raw acetylene and dissolved air is pumped out. Next the second cylinder is evacuated and then cooled in a LN2 bath. The first cylinders temperature is then raised to ≈ 170 K and the two cylinders commonized. The acetylene preferentially transfers to the second cylinder due to it's higher vapor pressure. After the acetylene is transferred, the acetone is disposed of and another purification cycle can begin.

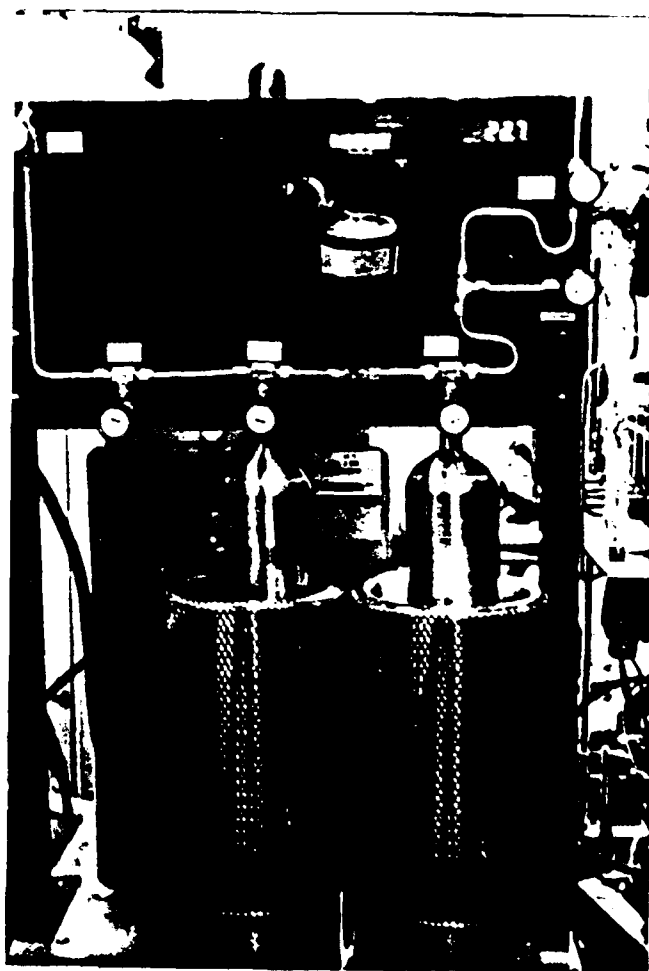


Figure 5. Cryogenic acetylene purifier.

Samples of the raw and the purified acetylene were passed through ORBO 91 sampling tubes and then the tubes were sent out for gas chromatography analysis. Coupling the sampling capacity of the tubes with the sensitivity of gas chromatography should give a detectability of acetone in the acetylene of ≈ 10 ppm.

Preparation of trenched Si substrates. To study ALE of SiC in trenches, a program for producing trenched substrates has been started. The substrates would be processed using oxidation, photolithography and reactive ion etching (RIE) equipment in the microelectronic fabrication facility at N.C. State University. The substrates would be processed in the following manner explained graphically in Fig. 6.

Prepare all wafers.

1. RCA clean Si(100) substrates oriented 3° off axis toward $\langle 011 \rangle$.
2. Dry-wet-dry oxidize substrates to form $\approx 5000\text{\AA}$ of SiO_2 .

Determine oxide etch rate.

3. Reactive Ion Etch, (RIE), oxidized Si wafer in SiF_4 and O_2 atmosphere to determine the oxide etch rate by measuring oxide thickness with ellipsometer before and after etch.
4. Spin photoresist onto remaining wafers.

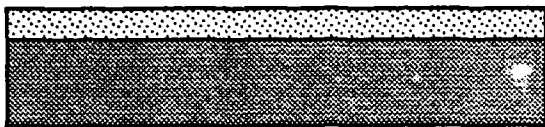
Determine Si etch rate.

5. Using a standard mask and developing procedures, open large holes in photoresist on test wafer(s).
6. Use HF to remove exposed oxide.
7. Remove all remaining photoresist.
8. RIE test wafer.
9. Measure etched depth with Alphastep profilometer to get Si etch rate. The Si etch rate combined with the oxide etch rate will give the etch selectivity.

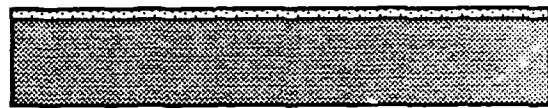
Process Remaining wafers.

10. Pattern and develop remaining wafers with custom mask to produce a set of openings 2.5, 5, 10, and 20 μm wide.
11. Use HF to remove exposed oxide.
12. Remove all remaining photoresist.
13. RIE wafers taking care to stop before going through all of the oxide.
14. Use HF to remove the remaining oxide.
15. Grow thin oxide ($< 500\text{\AA}$) on trenched wafers for passivation.

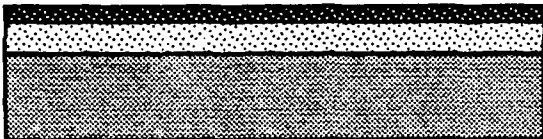
Deposition of non-stoichiometric SiC. Due to the possibility of bandgap engineering by varying the Si:C ratio in SiC films, two deposition runs were performed to produce SiC films for photoluminescence studies. Although both films were grown at 800°C under the pressure and same gas flow conditions, the rotation of the samples varied. The first film was exposed to



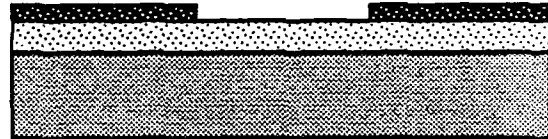
RCA clean and oxidize all wafers.



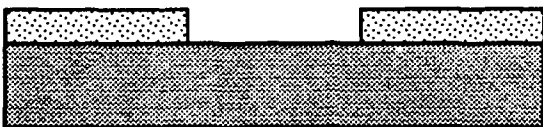
RIE test wafer(s) to find oxide etch rate.



Spin photoresist onto all oxidized wafers.



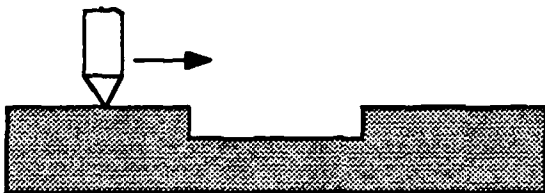
Open large holes in photoresist using a standard mask.



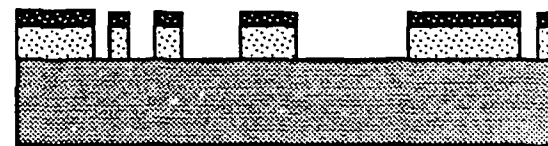
Remove exposed oxide and then photoresist.



RIE wafer.



Remove oxide and measure etch depth for Si etch rate.



Pattern remaining wafers with custom mask to make a series of openings. Remove exposed oxide and then remaining photoresist.



RIE patterned wafers and remove remaining oxide.



Reoxidize trench wafers for passivation.

Figure 6. Preparation of trenched wafers.

Si/C/filament/Si/C/filament ... for 530 cycles while the second film was exposed to Si/Si/Si/C/filament/Si/Si/Si/C/filament... for 530 cycles. The films were then examined using photoluminescence for bandgap measurement.

C. Results and Discussion

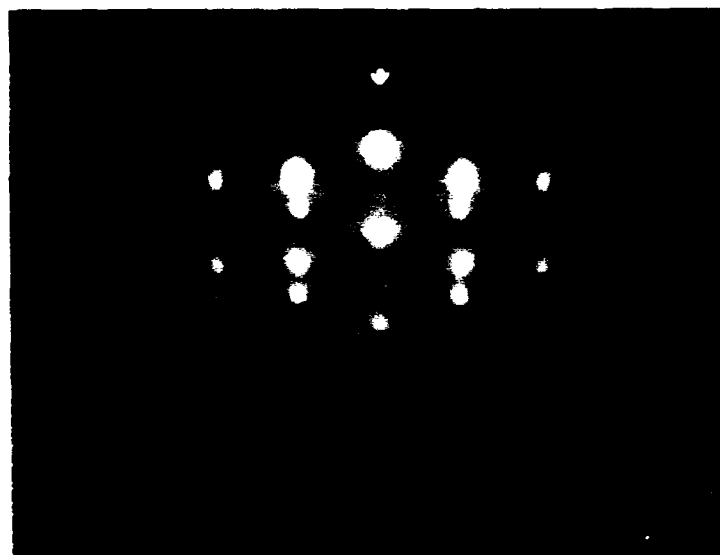
Minimum decomposition temperature of Si₂H₆ on $\alpha(6H)$ -SiC(0001) surface. After exposure to disilane for 1 hour at temperatures of 245, 300, 340, 430, 520 and 620°C, XPS was unable to detect any Si-Si bonding for samples processed at the three lower temperatures. Due to equipment difficulties, XPS analysis has not been completed for samples processed at 430, 520 or 620°C although there is a visible film on the 620°C substrate. At this time, it is expected that the minimal decomposition temperature for Si₂H₆ on the SiC surface, and the maximum temperature to form self-terminating monolayers, is $\approx 570^\circ\text{C}$.

Low temperature deposition of SiC. Figure 7 shows the [110] RHEED reflections of SiC films grown on the $\alpha(6H)$ -SiC(0001) surface using the low temperature rotation scheme. These films span a range of temperature from 500 to 850°C. It appears from the RHEED that the films are monocrystalline only for temperatures above 700°C. Although by more judicious selection of process variables, this temperature has been reduced slightly and the degree of preferred orientation of the polycrystalline films improved at lower temperatures, it has been impossible to deposit a monocrystalline film on SiC at temperatures commensurate with the established temperature ceiling for monolayer deposition from Si₂H₆.

Preparation of purified acetylene. Five batches of acetylene have been purified, sampled and sent off for analysis. The acetylene is guaranteed 99.6% pure before packaging in acetone and typically after the first cooling step about .3% of the raw gas is eliminated, probably as dissolved air. After the condensation transfer, about 2% of the original volume, probably acetone, is disposed of due to not transferring at cold temperatures. This is in agreement with typical published values of the amount of acetone impurity found in acetylene from bottles. Despite this circumstantial evidence that seems to indicate that the purifier is working well, the gas chromatography results should be definitive.

Preparation of trenched Si substrates. Thus far the wafers for trenching are on hand and the custom mask for making the trenches is on order.

Deposition of non-stoichiometric SiC. Two runs were completed to study the effect of non-stoichiometry on the bandgap of SiC. Both samples ran for 530 cycles. The first sample, exposed to a 1:1 ratio of Si:C, measured 1090 Å thick giving deposition of .94 monolayers per Si/C cycle. The second sample, receiving a 3:1 ratio of Si:C, measured 2083 Å thick giving a deposition of 1.8 monolayers per Si/Si/Si/C cycle. Confirmation of the actual Si:C ratio by auger spectroscopy for each film is underway.

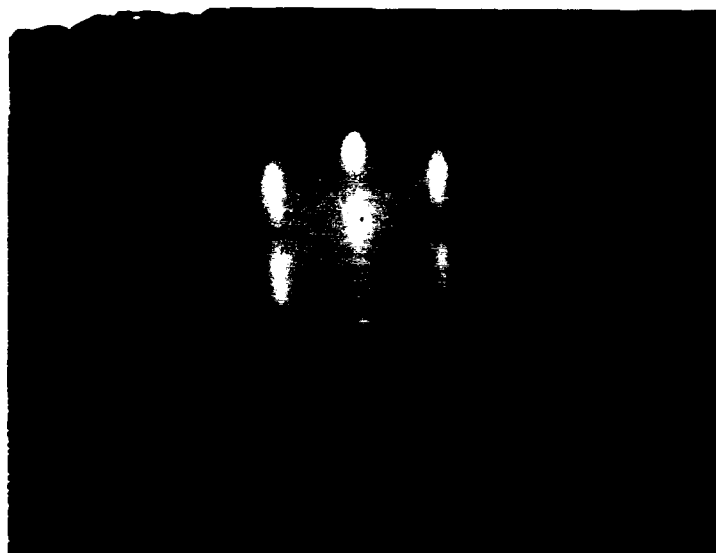


500°C

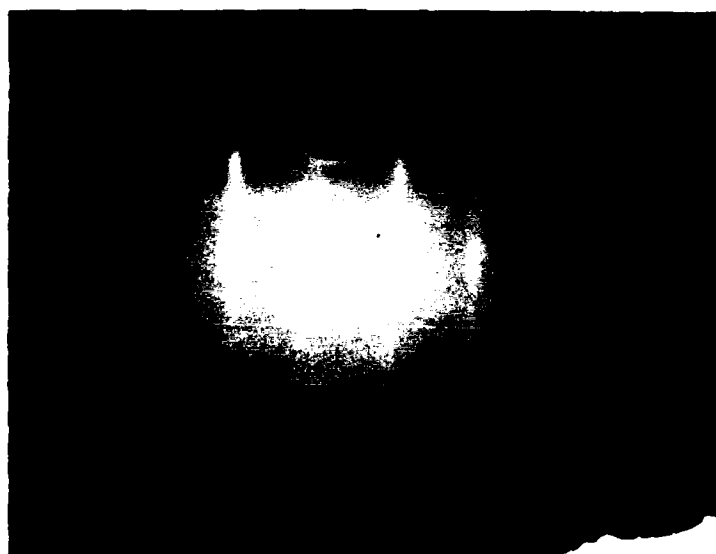


600°C

Figure 7. RHEED of SiC films deposited at low temperatures. [110] reflection.



700°C



850°C

Figure 7. Continued.

Photoluminescence studies of the two films revealed the spectra given in Figs. 8 and 9 for the 1:1 and 3:1 SiC films, respectively. Examination of the spectrum for the "stoichiometric" film gives a bandgap of ≈ 2.85 eV, while the spectrum for the "non-stoichiometric" film indicates a bandgap of ≈ 2.72 eV. The reduction in bandgap is expected for the Si rich film however the value of the bandgap for both films is unexpected.

As stated earlier, the bandgap of the 3C polytype of SiC, which all films grown in this project to date have been, is 2.2 eV. However, the most common polytype of SiC closely matching this value of 2.85 is the 6H polytype with a bandgap of 2.86 eV [10]. In an effort to determine the polytype of the deposited film, the x-ray diffraction pattern shown in Fig. 10 The peak at 69.14° corresponding to the Si(400) peak of the substrate is obvious and a peak at 65.8° is apparent. This 65.8° peak yields an interplanar distance of 1.43 \AA which would be found in the x-ray diffraction pattern of 6H-SiC but not in the pattern for 3C. However, due to the low intensity of the peak, this is not conclusive data.

At this point it would be premature to attempt to definitively identify the polytype of these samples as positive evaluation of these results by high resolution transmission electron microscopy is currently in progress.

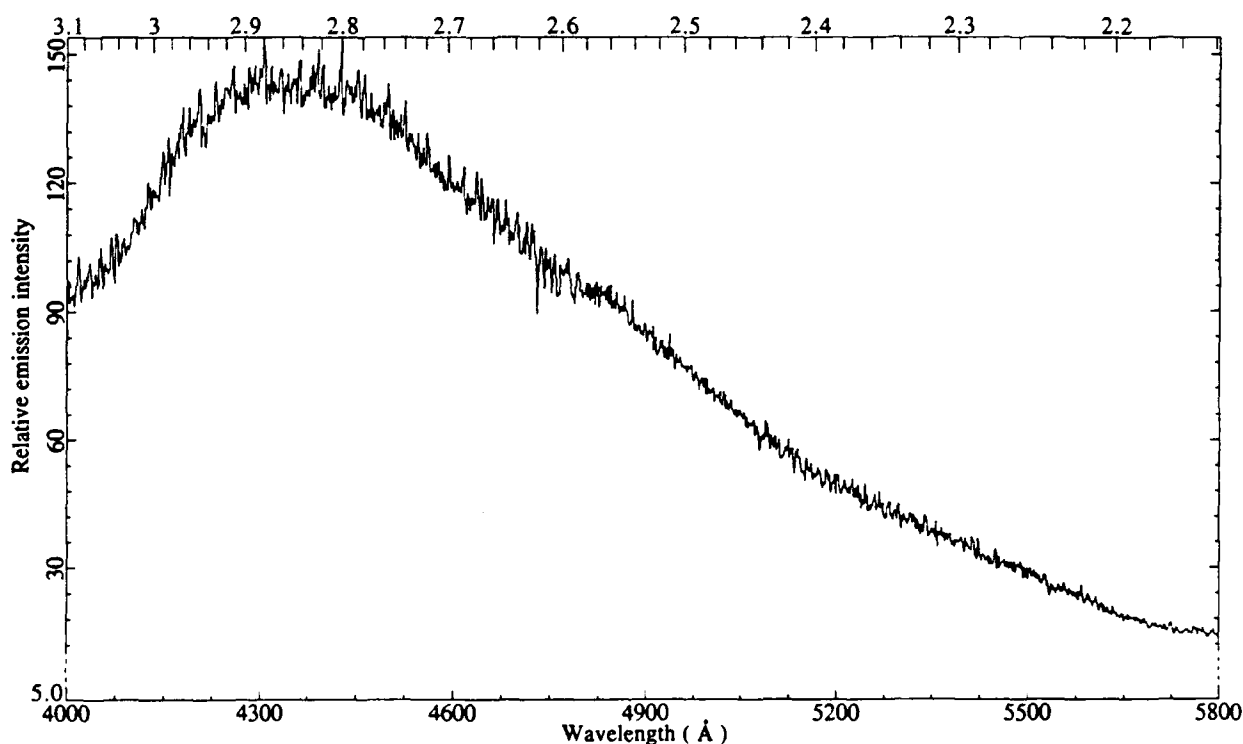


Figure 8. Photoluminescence spectrum of "stoichiometric" SiC film.

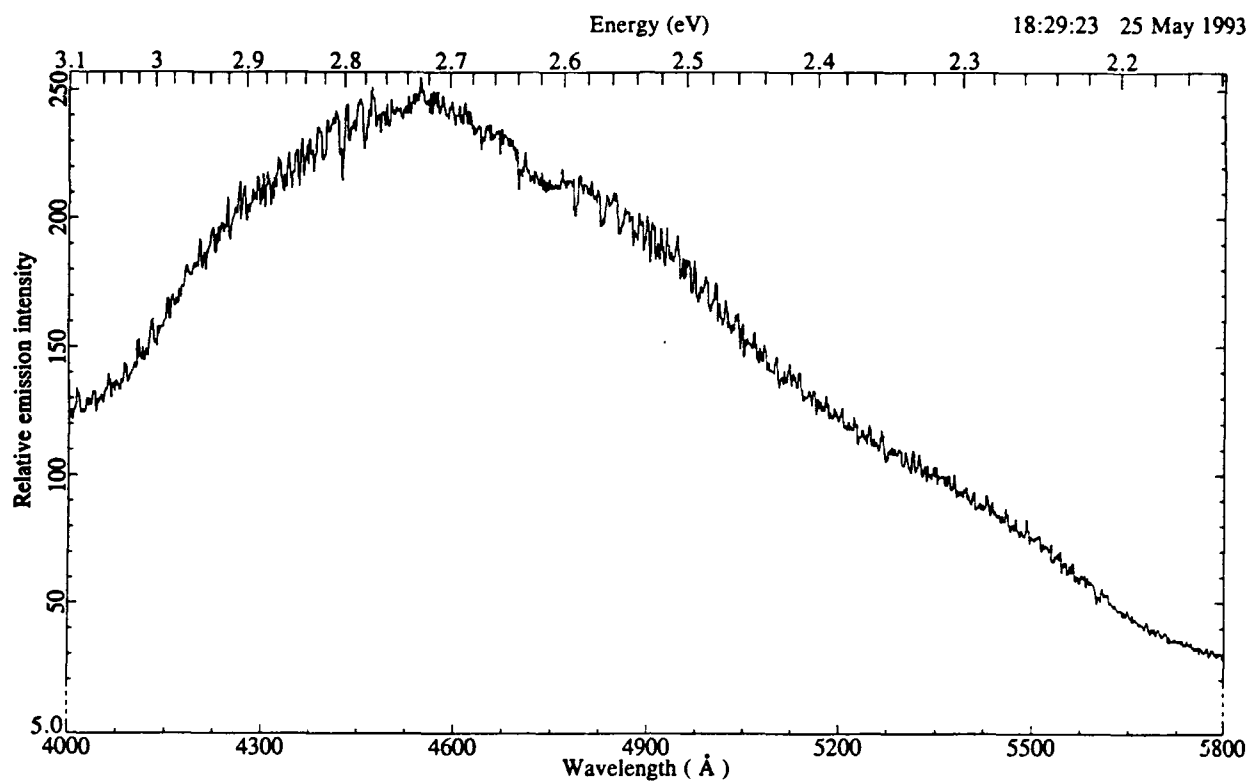


Figure 9. Photoluminescence spectrum of "non-stoichiometric" SiC film.

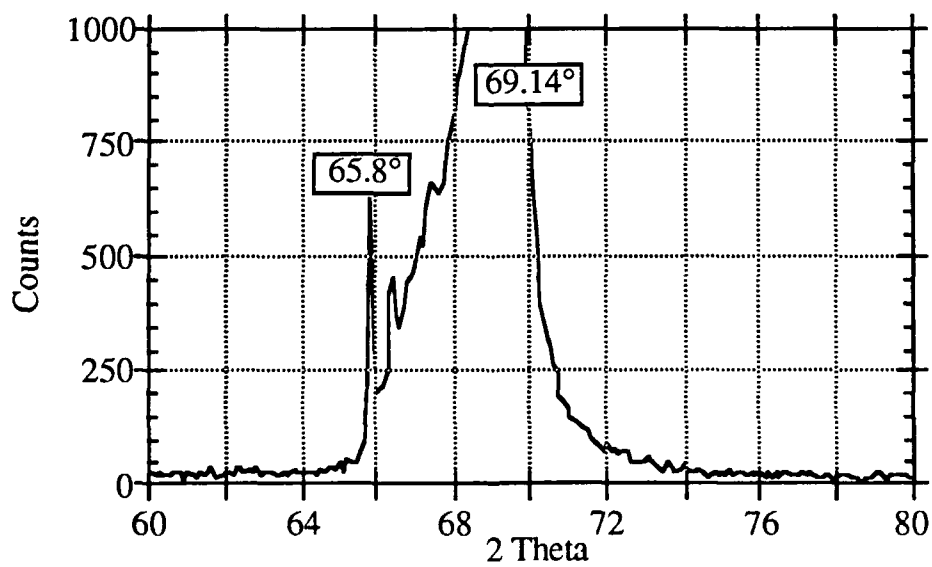


Figure 10. X-ray diffraction pattern from "stoichiometric" SiC film.

D. Conclusions

We have tentatively identified the maximum temperature at which self terminating monolayers of Si can be formed from Si_2H_6 on a SiC surface as 570°C , but certainly no higher than 620°C . Considering these temperatures as temperature ceilings for depositing SiC in a self-limiting ALE process, we cannot deposit monocrystalline films in a true ALE fashion using our current materials. Acetylene gas has been chosen as a successor due to its superior reactivity and chemisorption properties in comparison to ethylene. A purifier for removing acetone from acetylene has been commissioned, and samples of purified gas sent for analysis.

Work is in progress to produce trenched Si substrates to assess the deposition of SiC within trenches by our layer-by-layer process and eventually by an ALE process.

The effect of non-stoichiometry on the bandgap of deposited SiC films is being studied. The first set of experiments has revealed a decrease in bandgap with increasing exposure to Si_2H_6 during deposition. However, anomalous bandgap values for the films raises some question as to the polytype of the films. Auger chemical spectroscopy and high-resolution transmission electron microscopy work are in progress to definitively determine the composition of the films and the polytype.

E. Future Research Plans

1. Complete analysis of non-stoichiometric films.
2. Extend non-stoichiometric film work to attempt to extrapolate data on SiC bandgap as a function of composition.
3. Once assured that acetylene purifier effectively removes acetone, resume work trying to deposit SiC in a self-limiting ALE fashion.
4. Complete trenching Si wafers and address the ability to deposit SiC in trenches etched in Si wafers.
5. Attempt to dope SiC films with Al and N.
6. Employ the ALE technique for construction of multilayers and solid solutions of the SiC-AlN system.

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III. Integrated Surface Science System for Studies of the ALE of SiC

A. Introduction

In this report period, a concentrated effort has been made at completing assembly and construction of both an AES/XPS UHV analytical system and an associated ALE growth system. Much effort has also been spent in integrating these two systems into a much larger surface science system here at NCSU which has such capabilities as AES, AR-UPS, LEED, MBE, *in-situ* Raman, and Hydrogen Plasma Cleaning. Integration of all these separate systems will allow a very thorough study and characterization of both the initial nucleation of SiC (i.e. first few reaction cycles) and the overall ALE growth process of SiC.

B. Results

AES/XPS system. Completion of the construction and assembly of the AES/XPS UHV analytical system has been completed. The UHV system is capable of pressures in the 10⁻¹⁰ torr regime with the aid of both a 220 l/s ion pump and a Titanium sublimation pump. The AES/XPS system is composed of a VG LEG 62 electron gun, a VG XR3E2 x-ray source, and a VG CLAM-II hemispherical electron energy analyzer. Preliminary testing of the system has been performed on Au, Cu, and SiC samples with reasonably satisfactory spectrums being obtained in all cases indicating that the system is in good operational order. In order to perform both angle resolved AES and XPS, a manipulator with 5 degrees of freedom has been constructed. Two of the degrees of freedom (i.e. the necessary theta and phi rotations) were designed to be controlled by stepper motors. Control of these stepper motors has been achieved through the use of a special card purchased from Keithley-Metrabyte Asyst and has also been tested.

ALE Growth Studies System. Completion of the growth system for the ALE of SiC has also just recently been completed. This system is actually a combined growth and analysis system with capabilities of performing adsorption kinetic studies, temperature programmed desorption (TPD), sub-monolayer gas dosing, and thick film growth (>20 nm). The growth studies system contains a Hiden Analytical Quadrupole Mass Spectrometer (HAL 201) and associated Hiden TPD hardware and software which allows the QMS to be used in remote operation by a computer for both TPD and gas adsorption studies. The QMS is currently operational and the integration of the TPD hardware and software with the sample heating system is currently in the debugging stage. Two gas dosers have also just recently been installed on this system with each doser being dedicated to a separate gas. The dosers are of the same design as the molecular beam dosers used by Dr. Yates at the University of Pittsburgh. [1] After much consideration, the gases which have been selected for use in these

studies are Si_2Cl_6 and C_2H_2 . Selection of these gases was based primarily on the excellent results of both Dr. Gates (IBM Watson) [2] with regards to Si_2Cl_6 and Dr. Yates (U. Pittsburgh) [3] with regards to C_2H_2 . The Si_2Cl_6 has just recently been purchased and received from Cambridge Isotopes. The C_2H_2 will be obtained from the purification system currently in place on the separate SiC ALE reactor here at NCSU. The molecular beam dosers that are a part of this growth studies system will be used for both sub monolayer experiments and thick film growth. Sub monolayer exposures will be achieved via these dosers by restricting gas flow to occur through a laser drilled micron-sized orifice in a blank VCR gasket as with Dr. Yates' dosers. In order to achieve thicker film growth within a reasonable period time, the VCR gaskets with the micron sized orifices will be replaced with VCR gaskets which have a much larger orifice drilled in them (i.e. 0.1–5 mm). These gaskets are easily interchanged without having to bring the entire system up to atmospheric pressure as Nupro valves have been placed on both system side of the gasket and the gas line side of the gasket. The vacuum in this system should also not be jeopardized due to the resulting higher gas loads from the larger gaskets as the system has been equipped with a 500 l/s Varian ion pump, 400 l/s Leybold turbo pump, and a titanium sublimation pump. Currently this system has reached the high 10^{-9} torr regime with no bake out and is expected that 10^{-10} torr will be easily reached after bake out.

NCSU Surface Science System. The two previously mentioned UHV systems have been integrated with one another by connecting them to the larger NCSU Surface Science System. The NCSU Integrated Surface Science System brings together a variety of independent surface science systems (with support from both different ONR and other on-going programs) and is under the direction of Dr. R. J. Nemanich. Previously, the NCSU ISSS consisted of separate systems with the following capabilities: AR-UPS, AES/LEED, MBE, *in-situ* Raman, and Hydrogen Plasma Cleaning. The crux of this system is the long UHV transfer line (approximately 30 ft.) to which a variety of separate UHV systems are connected via ports perpendicular to the longitudinal axis of the transfer line (Fig. 1). This setup allows each UHV system to easily access all the other UHV systems with transfer times normally less than five minutes. As the pressure in the transfer line is currently nominally in the 10^{-9} region, this setup allows a variety of different experiments to be done *in-vacuo* eliminating contamination of samples by ambient conditions.

C. Discussion

The aim of the future research will be to utilize the newly completed AES/XPS and ALE growth systems to study the initial steps of a SiC ALE process (i.e. first few monolayers of growth). Advantage will also be taken of the analytical and cleaning techniques available as a result of being a part of the larger NCSU Surface Science System (i.e. UPS, LEED, and Plasma Cleaning). All of these available analytical techniques will be used to study each step

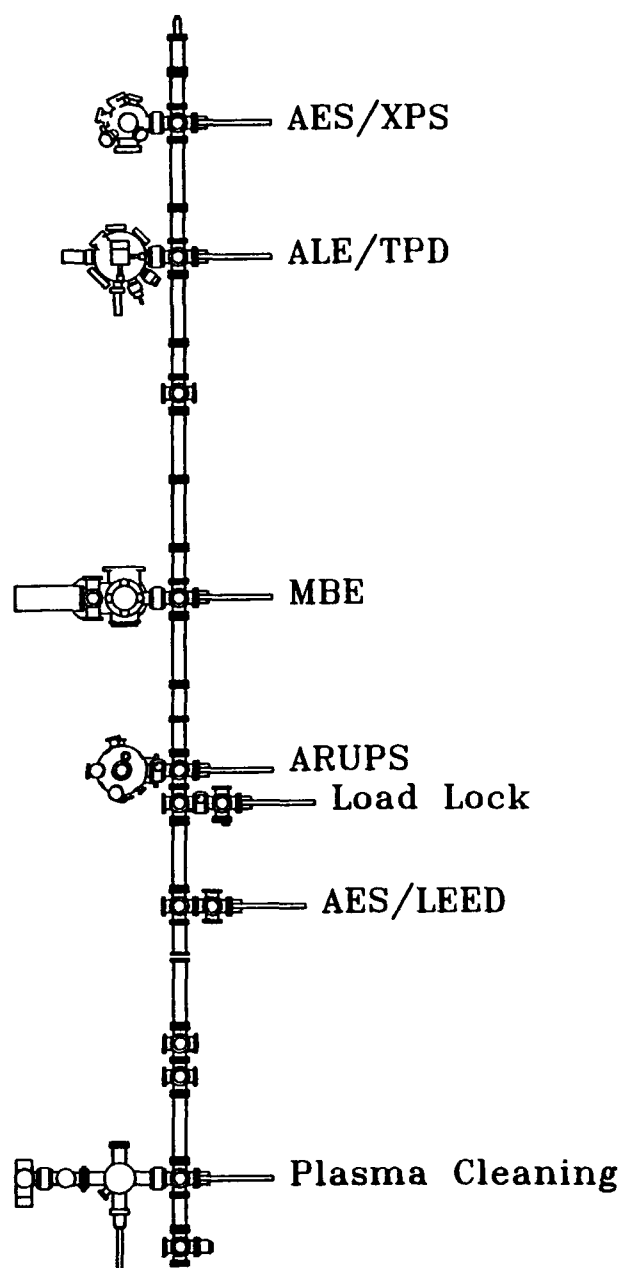


Figure 1. NCSU integrated surface science system.

(and fraction of steps) of the ALE of SiC and the information gained from each technique will be combined with those from others to paint a sort of mosaic picture of the ALE of SiC.

Before any experiments are done which are directly pertinent to the ALE of SiC some initial experiments will be done to try and find the best *ex-situ* and *in-situ* methods of cleaning Si and SiC which are compatible with our setup. In order to characterize the cleanliness of the wafer's surface, both the AES/XPS and AES/LEED systems will be used and possibly the UPS. These three systems should characterize our cleaning process by identifying surface contaminants (AES/XPS/UPS), assessing surface order (LEED), and determining the chemical nature of the

surface carbon (XPS). TPD may also be used to determine the nature of any adsorbed contaminants as well as to see if the cleaning process has left a hydrogen terminated surface or residual hydrogen in the bulk of the crystal. These studies will be important for two reasons. First, in order to study in detail the underlying processes of ALE of SiC, one must have a well defined starting point with which one can consistently return and make reference to. Obviously, a clean Si or Si terminated SiC surface is the best reference point for these studies. Secondly, the above experiments will serve as a means of fine-tuning and calibrating the newer analytical techniques (i.e. AES, XPS and TPD).

Once suitable methods are obtained for cleaning Si and SiC which are reproducible and well characterized by the available analytical techniques, the focus of the research will quickly turn toward looking at the adsorption of Si_2Cl_6 on both Si and Si terminated SiC (001). The first experiments performed will be kinetic uptake measurements similar to those of Yates [3]. Ideally, these experiments would be followed by LEED, AES, XPS, UPS, and finally TPD. The logistics of the ISSS transfer system may suggest a different sequencing of these experiments, however, the ultimate combination of all these techniques will provide such information on:

- The temperature range over which chemically self terminating monolayers of Si_2Cl_6 can be adsorbed to Si and SiC.
- How the Si_2Cl_6 adsorbs (i.e. molecularly or dissociatively)
- The sites at which Si_2Cl_6 might adsorb
- The amount of Chlorine that remains on the surface.

In short, these sets of experiments should provide vital information on the first step of an SiC ALE process where Si_2Cl_6 is the process gas.

On completion of the Si_2Cl_6 adsorption studies, more ALE type studies will be performed in which C_2H_2 will be brought in to interact with adsorbed monolayers of Si_2Cl_6 . These studies will be performed in exactly the same fashion as those for Si_2Cl_6 except instead of starting with a clean Si or Si terminated SiC surface a surface pre-exposed to Si_2Cl_6 will be used.

D. Conclusions

Both AES/XPS and ALE growth system have been established for the studies of the ALE of SiC. These two systems have been fully integrated with the NCSU Integrated Surface Science System allowing for a wide variety of analytical techniques to be employed on a single problem. This capability will enable a much better picture of the epitaxial growth of SiC (by ALE, MBE, etc.) to be painted, thus allowing the improvement of SiC epitaxial processes.

E. Future Research Plans and Goals

1. Characterize the *in-situ* and *ex-situ* cleaning process for SiC wafers.
2. Perform adsorption, TPD, AES-XPS, UPS, and LEED studies on the initial adsorption of Si₂Cl₆ on both Si and SiC (001).
3. Study the interaction of C₂H₂ with adsorbed Si₂Cl₆ monolayers.

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IV. Diamond Nucleation with Organosilicic Species

A. Introduction

Since the June 1992 report, diamond film quality on single crystal silicon substrates using HMDS precursors has improved greatly. Previous diamond films using HMDS exhibited poor quality diamond-like carbon although with high nucleation densities.

Current films show good quality diamond with high nucleation densities, as determined by Raman spectroscopy and SEM, respectively. TMS has also been shown to produce good quality diamond films.

An electron gun has been installed on the integrated UHV growth/analysis system (Fig. 1), described in the December 1992 report, to allow for Auger electron spectroscopy. The current experiments are being conducted in the stand-alone CVD chamber to avoid contaminating the new CVD growth chamber attached to the UHV analysis system with many different organometallics. When a suitable species is found, the experiments will be moved to the UHV growth chamber. A heating stage has been added to the stand-alone chamber to allow substrate heating during organometallic deposition.

B. Experimental Procedure

Substrate Cleaning. One inch diameter Si <111> wafers, 10–12 mils in thickness, are spin etched according to a procedure developed by Fenner [1]. The cleanliness of the wafers is confirmed by XPS (Figs. 2a,b,c). Very small amounts of carbon and oxygen are detected on the surface of a spin etched wafer. The silicon surface remains passivated with hydrogen long enough for the wafer to be loaded into the CVD chamber. The chamber is then purged with argon and pumped down to a pressure of 10^{-6} Torr within 15 minutes.

Si <111> wafers are used since the (111) surface has only one perpendicular dangling bond per surface cell [2] and thus offers the least steric hindrance for adsorbing molecules. The surface passivation ensures that Si dangling bonds are available to react with the adsorbing species. Without passivation, surface contamination would interfere with the surface/species reaction.

Organometallic Deposition. An in-line injection port has been placed into the carrier gas line feeding into the CVD chamber. A gas chromatograph type syringe is used to inject precise amounts of organometallic species into the carrier gas stream through the injection port. Volumes as small as 0.5 μL can be injected. Helium is used as the carrier gas and the deposition pressure is 20 Torr. The carrier gas lines are heated and their temperature can be varied according to the organometallic species used so as to keep the species from adsorbing onto the tubing walls.

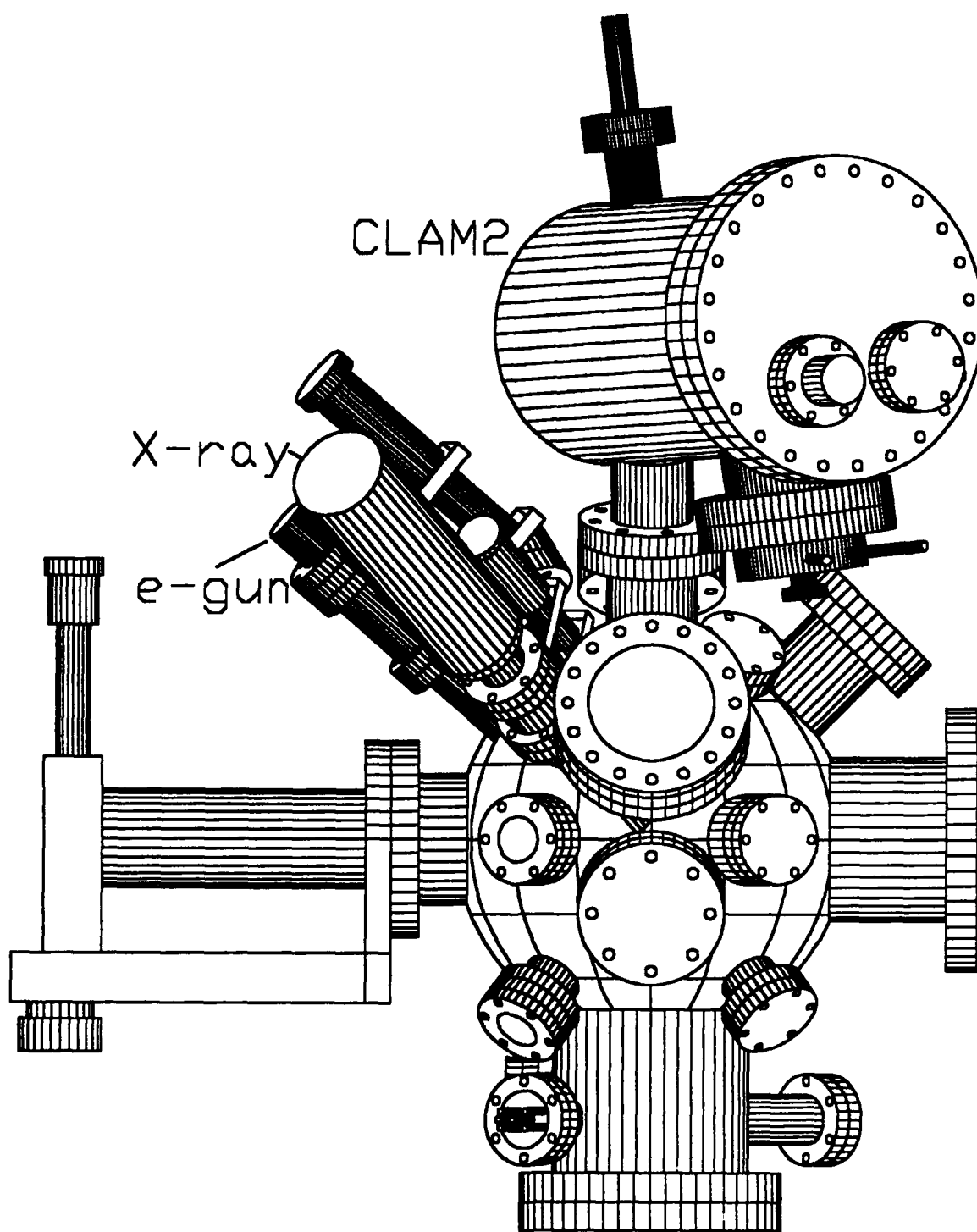


Figure 1. Diagram of the analytical chamber which includes X-ray photoelectron spectroscopy and Auger electron spectroscopy.

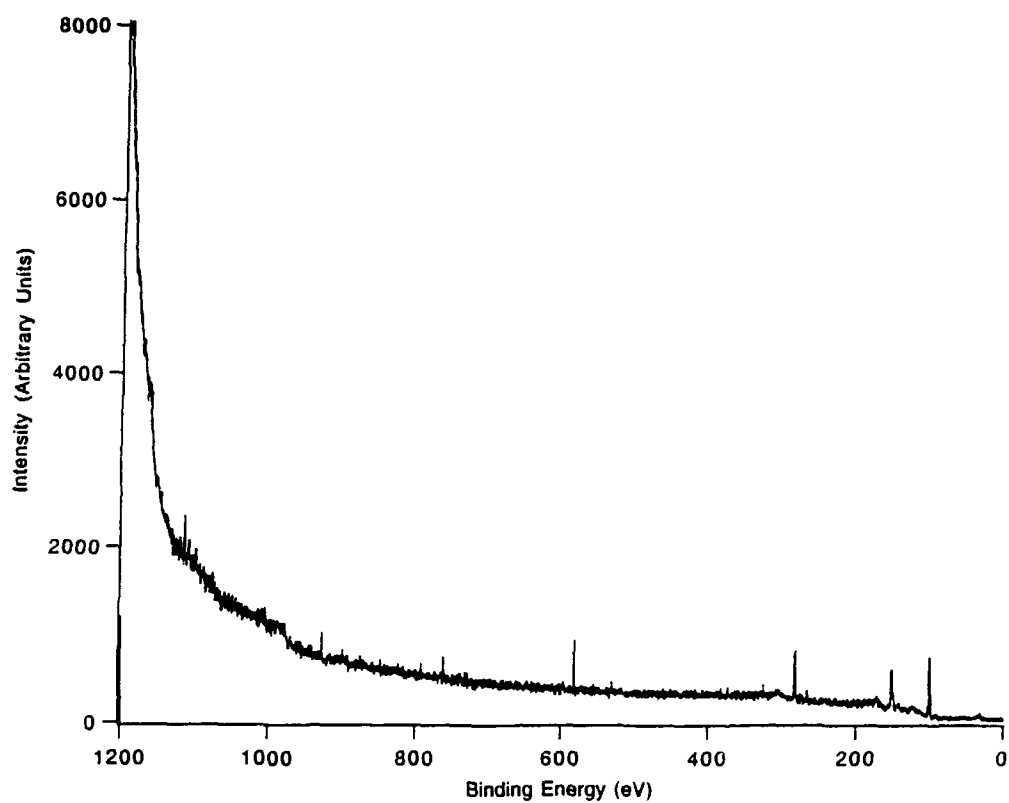


Figure 2a. XPS survey scan of Si <111> substrate cleaned by spin etch method.

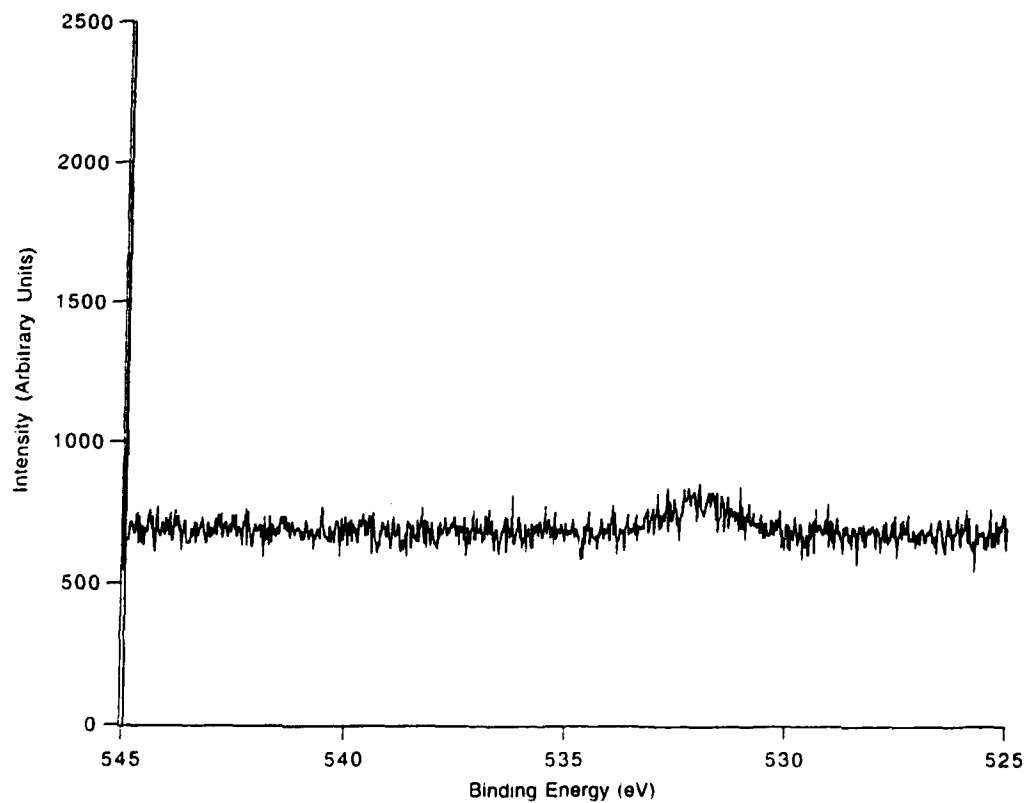


Figure 2b. XPS Oxygen 1s scan of Si <111> substrate cleaned by spin etch method.

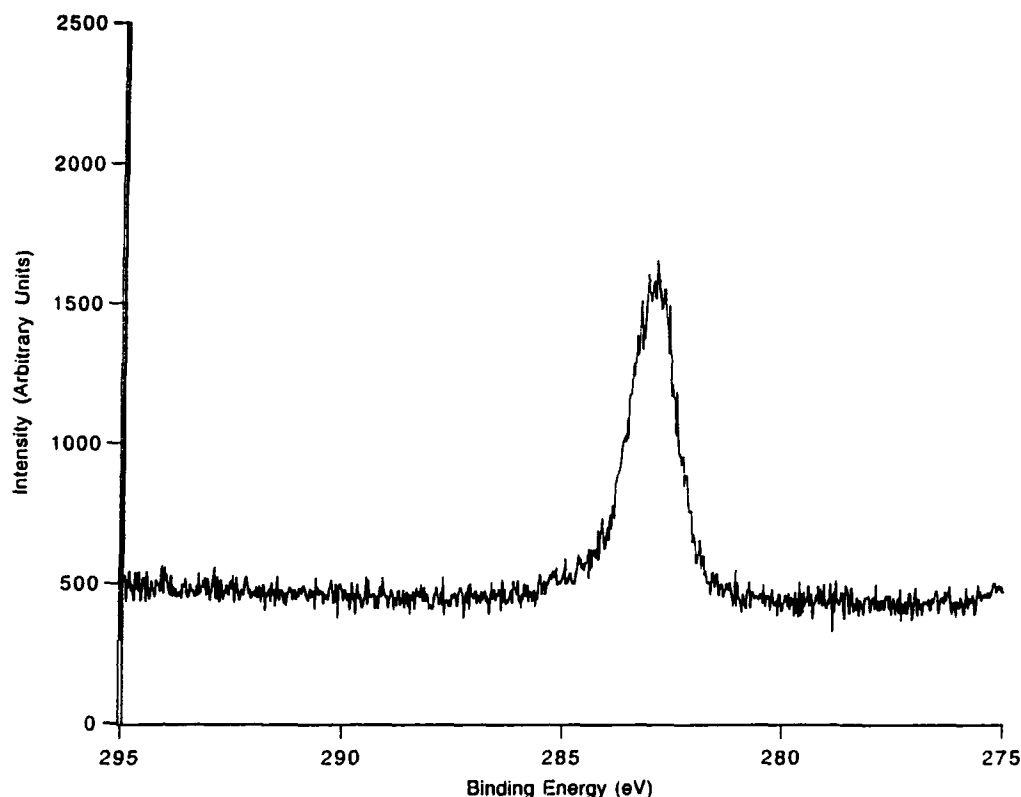


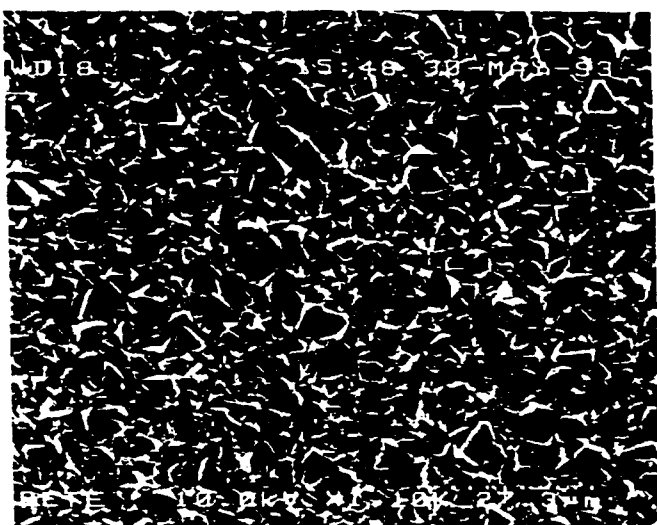
Figure 2c. XPS Carbon 1s scan of Si <111> substrate cleaned by spin etch method.

Diamond Growth. After deposition of an organometallic species, the He carrier gas is shut off and if the substrate heater is being used, it is turned off. H₂ gas is admitted into the chamber, and the CVD filaments are switched on. At a substrate temperature of approximately 600 °C, the CH₄ is switched on and the CH₄/H₂ ratio is adjusted to give a total flow rate of 300 sccm with a CH₄ in H₂ concentration of 2%. A growth pressure of 30 Torr is used in the current experiments. Reverse DC biasing of the substrate is used to attract cationic species created by the pyrolysis of the CH₄ and H₂. The bias voltage is 250–300 volts and the current is 100–200 mA.

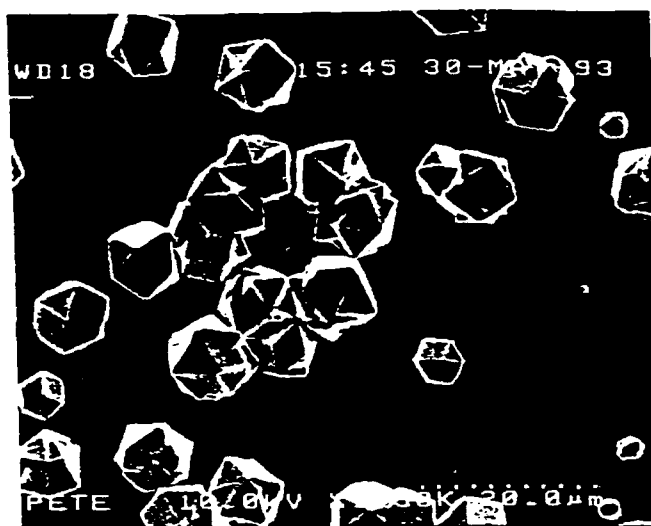
Growth times of 4 hours were first used in order to observe the early stages of diamond nucleation. However, in many cases a complete film of diamond is observed to cover the substrate within that time. Growth times of 40 minutes were then used.

C. Results and Discussion

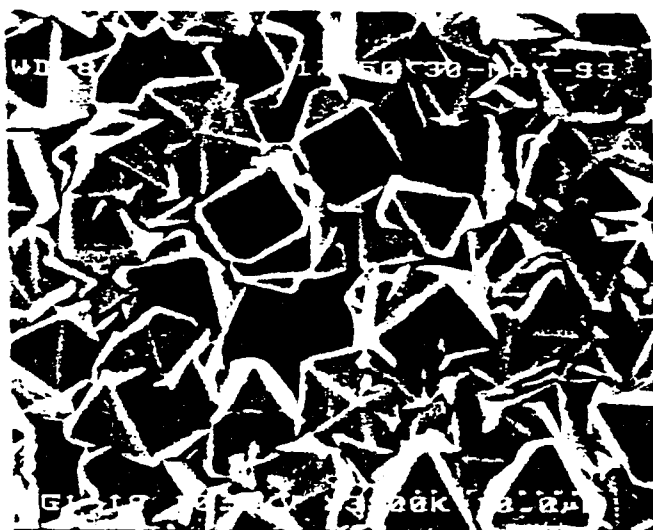
HMDS. Depositing the HMDS at a substrate temperature of 600 °C leads to better quality diamond films as opposed to diamond films produced when depositing HMDS at room temperature. The diamond film on the substrate which was heated prior to HMDS deposition is good quality (Figs. 3d and 4c), while the film on the substrate unheated prior to HMDS deposition is poor, diamond-like carbon.



a.



b.



c.



d.

Figure 3. SEM micrographs of diamond films deposited on Si $\langle 111 \rangle$ substrates.
a. untreated wafer, b. particles on untreated wafer, c. TMS treated,
d. HMDS treated.

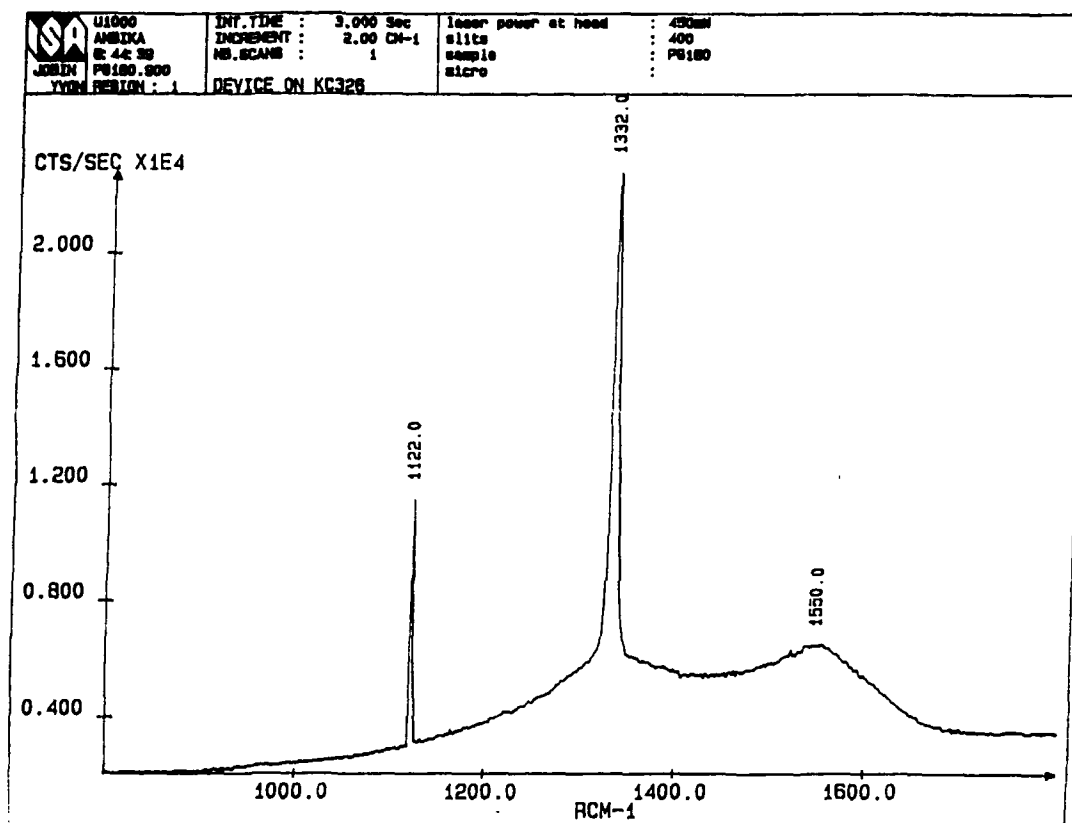


Figure 4a. Raman spectrum of diamond film on untreated Si <111> substrate.

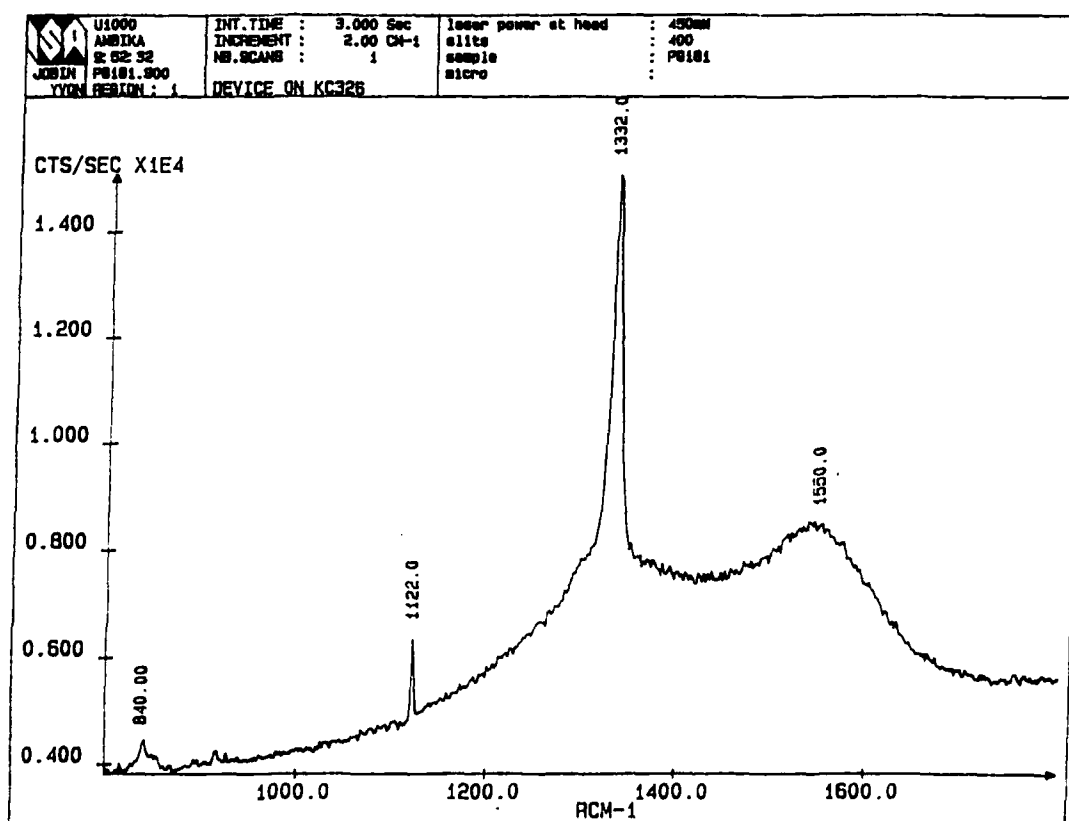


Figure 4b. Raman spectrum of diamond film on TMS treated Si <111> substrate.

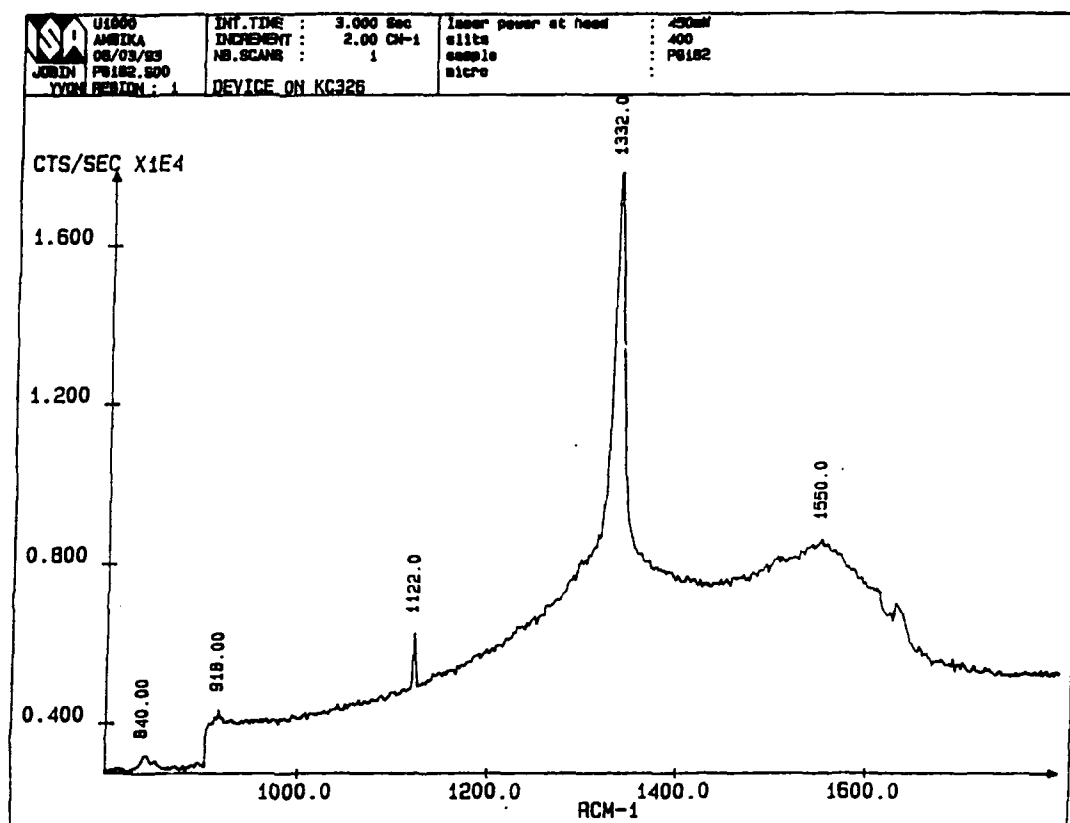


Figure 4c. Raman spectrum of diamond film on HMDS treated Si <111> substrate.

The diamond nucleation density of the HMDS treated substrate is greater than that of the untreated substrate. The diamond film quality, however, on the untreated substrate is better as shown by the Raman spectra. This is believed to be due to excess carbon on the substrate surface.

TMS. Diamond films grown on substrates on which TMS is deposited exhibit good quality (Fig. 4b), highly faceted films (Fig. 3c). The nucleation density appears to be slightly less than that produced by the HMDS.

Comparison of HMDS and TMS with an untreated wafer. The diamond film quality of wafers treated with HMDS and TMS are very similar (Fig. 4b,c). This is not surprising if there are many molecular layers of species present in the interlayer. Since both HMDS and TMS are highly substituted with methyl groups, there will be an abundance of methyl groups in many orientations. These amorphous regions probably catalyze the formation of graphite.

A sample with no organometallic deposition is subjected to the same growth conditions as the wafers with HMDS and TMS. SEM shows a slightly lower nucleation density for the untreated wafer (Fig. 3a,b), but the diamond quality as determined by Raman spectroscopy is better (Fig. 4a). The FWHM of the 1332 cm^{-1} diamond peak is narrower and the sp^2 peak is smaller.

Previous experiments in hot-filament biasing have shown that biasing results in a deposit which has a circular region beneath the filament with lower nucleation density. This is an effect believed to be the result of the orientation of the electric field lines. Fig. 3a is a SEM micrograph of the untreated wafer outside of this circular region and a complete film has developed. However, Fig. 3b is a micrograph of the same sample in this circular region where particles may be seen and the nucleation density is much lower. Thus, in order to compare nucleation densities, Figs. 3b, c and d were all taken in this same circular region.

The reason the diamond film quality on the untreated wafer is better than those wafers treated with HMDS or TMS appears to be due to an excessively thick interlayer. While we have vastly improved our organometallic deposition process, we still have not yet reached monolayer control of the species deposition. Further work on controlling the process will be needed.

D. Conclusion

Good quality diamond films have been nucleated on HMDS and TMS deposited interlayers. The organometallic deposition system has been improved to allow better monolayer control of the deposition process, and, in future experiments, monolayer control will be attempted. An Auger electron gun has been added to the UHV growth/analytical system to enable AES. To allow substrate heating during organometallic deposition, a heating stage has been installed in the UHV growth chamber.

E. Future Work

We have now gained control of the amount of organosilicic species through use of a syringe injection mechanism. The next step will be to compare the effects on nucleation density of methyl-to-silicon ratios by using the following organosilicic species:

| | |
|------------------------|-----------------------------------|
| tetramethylsilane | $(\text{CH}_3)_4 \text{ Si}$ |
| chlorotrimethylsilane | $(\text{CH}_3)_3 \text{ Si Cl}$ |
| dichlorodimethylsilane | $(\text{CH}_3)_2 \text{ Si Cl}_2$ |
| methyltrichlorosilane | $(\text{CH}_3) \text{ Si Cl}_3$ |

The species which gives the highest nucleation density will then be chosen as the most likely candidate for ALN, and we will begin to look at parametric space design (using SED software) to determine the optimum values of the following parameters: injection temperature, growth temperature, injection amount, methane percentage, injection pressure, and growth pressure. A cooling stage will be used to ascertain whether diamond deposition is enhanced at lower substrate temperatures using an organosilicic species. Also, we will determine whether

the carrier gas for the organosilicic species (i.e. helium versus hydrogen) affects the deposition. Further, we will be assembling a Helium-Neon laser interferometry system to monitor *in-situ* growth of the films.

Presently, all experiments are being performed in a stand-alone chamber because we were uncertain if there would be any contamination problems. Once the organosilicic species is chosen and it is determined that there will be no wide-scale contamination problems, the experiments will be run in a hot-filament CVD reaction connected *in-vacuo* to Auger electron spectroscopy and X-ray photoelectron spectroscopy. With the assistance of these analytical techniques, determining monolayer coverage for the organosilicic species becomes possible. Once monolayer coverage is achieved, it will be possible to refine the parameter space to attempt two-dimensional nucleation of diamond.

F. Acknowledgements

Ambika Somashekhar and Professor Robert Nemanich for the measurement of Raman spectra. Also, we thank Kobe Steel, Ltd. for the use of their Field Emission Scanning Electron Microscope.

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V. Epitaxial Growth of CeO₂ on Si

A. Introduction

The growth of epitaxial ceramic thin films on silicon is of interest for applications to high quality silicon-on-insulator (SOI) layers and stable capacitor devices. CeO₂ is an excellent candidate for such an insulator, having the cubic fluorite structure, with the lattice misfit factor $\Delta a/a$ for CeO₂ to Si being 0.35%. [1] Also, CeO₂ has a dielectric constant of ~ 26 , which could potentially allow it to be used in stable capacitor devices of small dimensions. [1]

It has been shown that crystalline layers of CeO₂ may be grown on a Si substrate by means of laser ablation. [2,3] This process can be accomplished by irradiating a solid CeO₂ target with a high energy pulse from an excimer laser under ultra-high vacuum (UHV). This produces a "plume" of CeO₂ molecules free to move in UHV and form epitaxial layers on the Si substrate. By controlling the energy, frequency and length of the laser pulses, one hopes to achieve layer by layer growth of the oxide.

B. Experimental Procedure

Substrate Cleaning. Different cleaning procedures and variations thereof were tried in attempting to obtain an atomically clean Si surface prior to growth. The effectiveness of each procedure was evaluated by *in situ* reflective high-energy electron diffraction (RHEED). Specifically, chemical RCA cleaning was found to be only partially effective in obtaining a clean substrate. Due to the temperature limitation of $\sim 900^\circ\text{C}$ maximum for the heating station in the growth chamber, substrates cleaned by RCA method were left with islands of SiO₂ on the surface. Figure 1A shows a RHEED pattern of a Si (111) substrate cleaned by the RCA method. Spots indicate surface roughness. Similarly, variations of uv-ozone cleaning left undesirable island-type formations on the surface. However, when using a modified version of the RCA clean, a good 7×7 pattern was observed by RHEED, indicating a clean surface. Figure 1B shows a RHEED pattern of Si (111) substrate as cleaned by modified RCA.

Thin film deposition. There are many parameters which affect the quality, uniformity, and growth rate of thin films deposited by laser ablation. As mentioned above, a uv laser irradiating a solid target may form a "plume" of CeO₂, free to travel to the Si substrate in a UHV environment. This plume is typically gaussian in distribution, not unlike a full Knudsen cell one might find in a conventional MBE system. Figure 2 shows a schematic diagram of the components internal to the growth chamber. During growth the excimer laser was run at a charging voltage of 26kV, which produced an energy density of $\sim 160 \text{ mJ/cm}^2$ for the unfocussed beam. Pulse widths were 10 ns and repetition rates were varied between 2 and 5 Hz. The energy density arriving at the target was varied between approximately 2 and 10 J/cm^2 by means of a focussing lens. The target to substrate distance was varied between 2 and 7 cm. The target was 2" in diameter and commercially obtained with 99.9% purity.



Figure 1A. RHEED pattern of Si (111) substrate showing islands of SiO₂ on the surface.



Figure 1B. RHEED pattern of clean Si (111) substrate.

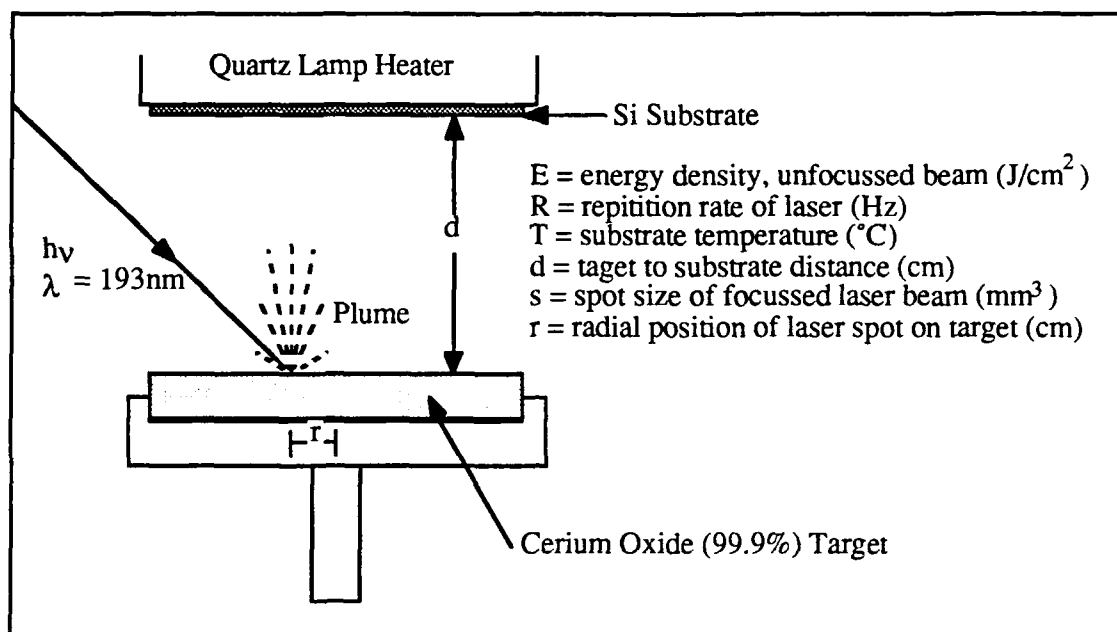


Figure 2. Schematic diagram of parameters affecting growth.

Substrates used in experiments were 2" Si (100) and 2" Si (111) wafers. Over a series of experiments, the substrate temperature was varied between $\approx 500^\circ\text{C}$ and 750°C as estimated by an optical pyrometer. Rotation of both the substrate and the CeO_2 target was employed to aid in achieving film uniformity. Limit vacuum before growth was 1×10^{-9} torr or better, and pressure during growth typically rose to $\approx 5 \times 10^{-8}$ torr due to outgassing of heated components and laser ablation. Growth runs contained between 10000 and 20000 pulses of the excimer laser.

Characterization of thin films. A quadrupole mass spectrometer (QMS) was used to detect residual gases and observe the oxidation state of the ablated CeO_{2-x} . During the runs, peaks at 140 amu, corresponding to Ce, and at 172 amu, corresponding to CeO_2 , were observed. *Ex situ* characterization methods include high-resolution transmission electron microscopy (HRTEM), ellipsometry to determine thickness of films, and x-ray diffraction.

C. Results

Crystalline Quality. Initially, all films were checked for quality by *in situ* RHEED analysis. This has proved to be a very powerful technique for quickly determining the success of an experiment at a very coarse level. From this data films could be sorted into 3 broad categories: polycrystalline, preferably oriented showing 2 domains, and highly oriented to epitaxial. Figures 3A and 3B show RHEED patterns of polycrystalline and epitaxial thin films respectively. *Ex situ* HRTEM and x-ray diffraction provided further insight to the growth process. Previous researchers reported an amorphous layer existing at the CeO_2 -Si interface, leading to preferred orientation polycrystalline films [3]. This type of amorphous layer is

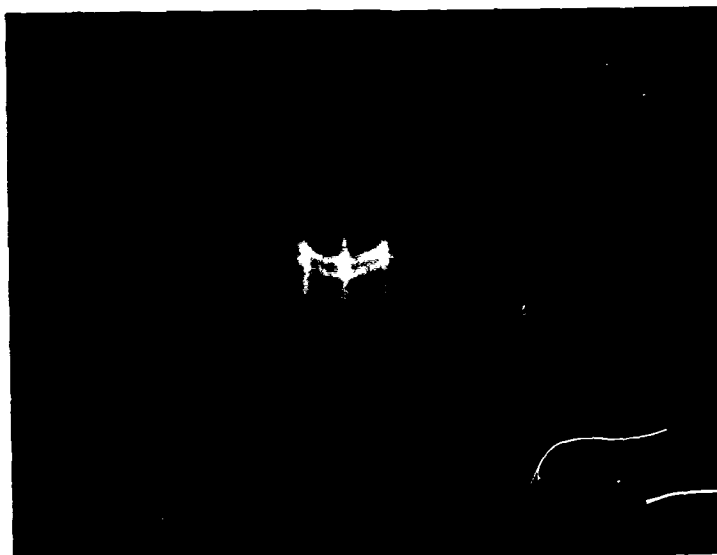


Figure 3A. RHEED pattern of polycrystalline CeO_2 on Si.



Figure 3B. RHEED pattern on epitaxial CeO_2 on Si.

shown in Fig. 4. However, we determined that this amorphous region need not exist. Figure 5 shows a crystalline CeO_2 -Si interface. This was achieved on an atomically clean Si substrate. Substrate cleanliness is therefore of great importance in achieving epitaxial growth. Figure 6 is an x-ray diffraction result indicating a single crystal film grown on an atomically clean substrate. For this system, crystalline quality was observed to increase at higher temperatures ($\approx 750^\circ\text{C}$), slower growth rates, and cleaner substrates.

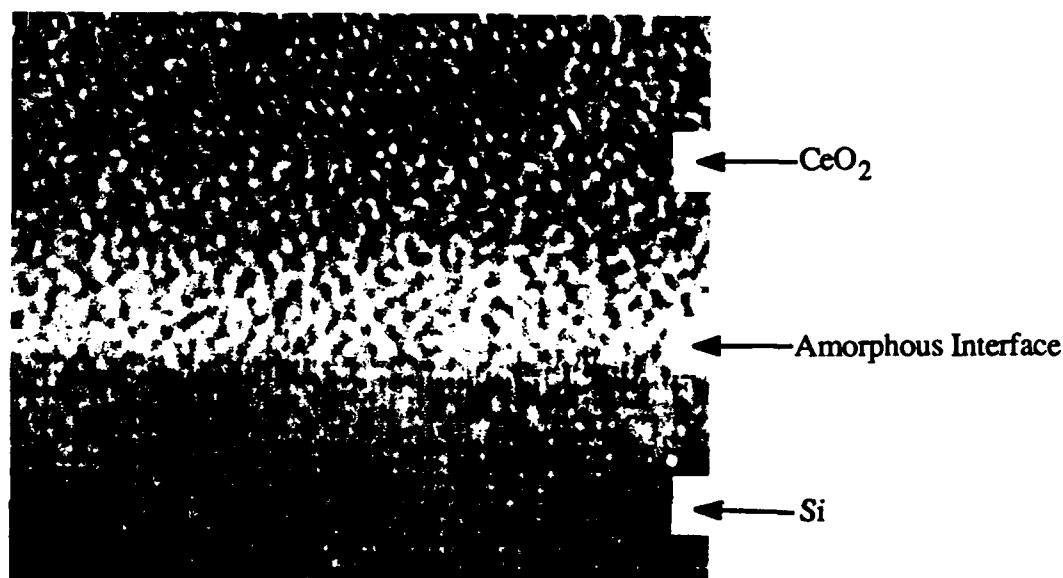


Figure 4. HRTEM micrograph showing an amorphous region at the Si (111)/ CeO_2 interface.

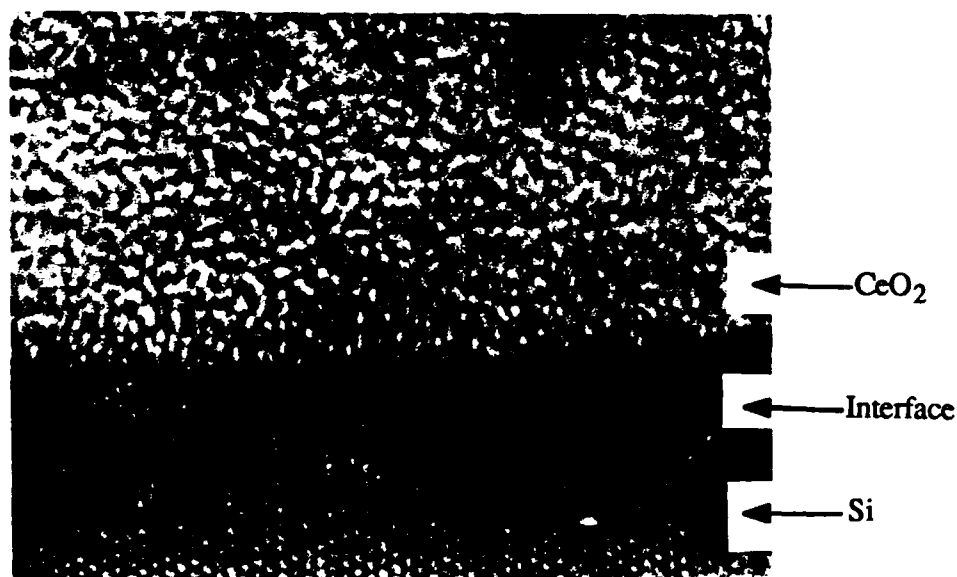


Figure 5. HRTEM micrograph showing a clean Si/ CeO_2 interface.

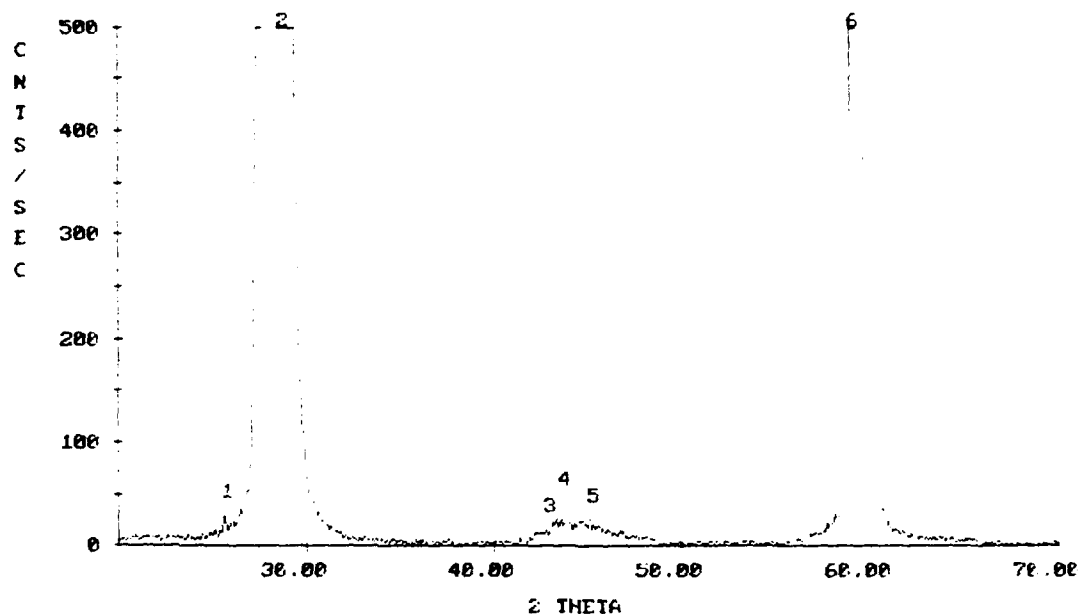


Figure 6. X-ray diffraction pattern indicating a single crystalline CeO_2 film.

Growth Rate. A goal of this research is to optimize the amount of CeO_2 deposited per laser pulse in order to achieve atomic layer epitaxy (ALE). Due to the gaussian nature of the plume ejected from the CeO_2 target, it is difficult to obtain uniform surface coverage of a 2" diameter substrate. In this system, it appears there is a trade-off between uniform coverage and the desirable ALE growth rate. In experiments performed with a stationary substrate, the maximum growth rate was observed to be 0.4 \AA per laser pulse. This is well below the theoretical ALE growth rate of 3.1 \AA per pulse. These experiments produced films ranging in thickness from 400 \AA to 4400 \AA , and uniform areas of $\approx 2 \text{ mm}$ in diameter. By rotating the substrate, films with uniform areas as large as 30 mm in diameter were epitaxially grown. Maximum growth rates for these experiments were 0.08 \AA per pulse. By combining substrate rotation, large target to substrate distance, and a large (defocussed) laser spot, uniform coverage of the entire 2" diameter wafer was achieved at a growth rate of 0.02 \AA per laser pulse.

D. Discussion

Determining the optimum growth conditions for a given system is an important step for research. For this particular system, the growth rate of CeO_2 is dependant on several parameters. The repetition rate of the laser determines the number of pulses per minute. The power of the laser and the focussing of the optical delivery system determine the amount of CeO_2 ejected from the solid target in the form of a plume per laser pulse. And the target to

substrate distance, the rotation of the substrate, and the radial distance of the plume position relative to the substrate (denoted as "r" in Fig. 2) affect the size of the area on the substrate covered by the plume. Substrate temperature does not affect the growth rate, since ablated CeO_2 may be assumed to have a sticking coefficient of 1, however, it does affect the crystallinity. Other researchers reported epitaxy of CeO_2 on Si (111) substrate as low as 200°C [7], however, we were unable to get good material below $\approx 600^\circ\text{C}$. Best results were achieved at $\approx 750^\circ\text{C}$.

A small variation in the excimer laser charging voltage leads to a large variation in the energy density of the laser beam. Therefore all experiments were conducted at a charging voltage of 26 kV, yielding $\approx 160 \text{ mJ/cm}^2$ for the unfocussed beam. The optical delivery system, however, was used to change the spot size of the focussed beam striking the CeO_2 target, thereby changing the energy density there. With the laser light perfectly focussed, a plume of CeO_2 was visible as each laser pulse struck the target. The plumes appeared to grow larger as the lens was defocussed up to a point, and then quickly disappeared. This observation can be explained by the threshold energy necessary to ablate CeO_2 . As the laser beam was defocussed, the area irradiated by the laser increased and the size of the plume increased, up to the point where the energy density fell below the threshold for ablation. Fastest growth rates occurred when the beam was slightly defocussed.

Crystal quality of ablated CeO_2 improved as the target-to-substrate distance (denoted as "d" in Fig. 2) increased, allowing the plumes to spread out and slowing the growth rate. Uniformity of the films also improves with greater d. However, as d increases, more of the plume misses the substrate and is lost. Experiments were run with d varying between 3 and 7 cm. A 5 cm target-to-substrate distance seems to offer the best trade-off between uniformity and growth rate, yielding a $\approx 3 \text{ cm}$ uniform area of excellent crystalline quality at a growth rate of $\approx 2.4 \text{ nm/min}$. With the rotating substrate, no difference in crystal quality was observed between experiments run with the laser repetition rate at 2 Hz and experiments run with the laser repetition rate at 5 Hz, even though the overall growth rate was increased. This is probably because consecutive plumes were not hitting the same area of the substrate as it rotated.

E. Conclusions

Good quality epitaxial films of CeO_2 have been grown on Si (111) substrate by a laser ablation method. Atomically clean substrates and slow growth rates are necessary for epitaxy.

F. Future Research Plans

Further investigation of the CeO_2 growth process is required. Specifically, characterization of electrical properties will be accomplished by capacitance-voltage measurements made on MOS

capacitors constructed on the grown films. This will enable us to optimize the growth parameters improve the electrical properties of epitaxial films.

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